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Bose-Einstein and Fermi-Dirac Distribution Laws

Bose-Einstein Statistics

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(19)

In the derivation of Planck's radiation formula, Bose utilised Planck's hypothesis of quantum theory, according to which a black body radiation chamber of volume V , is full of electromagnetic radiation of absolute tempⁿ T and in thermal equilibrium with the walls. An electromagnetic wave of frequency ν and velocity c consists of particles called photons of energy $h\nu$ and momentum $h\nu/c$. The cavity is assumed to be having a large number of photons, each one of them is indistinguishable from the others. The assembly of photons in the cavity may be compared to the assembly of gas molecule in vessels. Therefore, the assembly of photons is supposed to constitute a gas known as photon gas.

The phase volume associated with photons of frequency lying between ν_i and $(\nu_i + d\nu_i)$ is

$$G_{\nu_i} d\nu_i = \iiint \iiint \iiint dx dy dz \int dp_x \int dp_y \int dp_z$$

$$= \iiint dx dy dz \iiint dp_x dp_y dp_z$$

where the integration to be done within the frequency limits ν_i and $(\nu_i + d\nu_i)$

If V is the volume occupied by the photon gas in ordinary position space, then

$$\iiint dx dy dz = V$$

Now, at any instant, all photons having their momentum between p_i and $(p_i + dp_i)$ will lie within a spherical shell described in momentum with radii p_i and $(p_i + dp_i)$. The volume of this shell is given by,

$$\iiint dp_x dp_y dp_z = 4\pi p_i^2 dp_i$$

$$\therefore G_{\nu_i} d\nu_i = 4\pi p_i^2 dp_i V$$

Now, according to light quantum hypothesis of Einstein,

$$E = mc^2 = pc = h\nu$$

$$\therefore p = \frac{h\nu}{c} \quad \therefore dp = \frac{h}{c} d\nu$$

$$\therefore G_{\nu_i} d\nu_i = \frac{4\pi h^{\nu_i} \nu_i^{\nu_i}}{c^3} \cdot \frac{P_i}{e} \cdot d\nu_i \cdot V$$

$$= \frac{4\pi h^3 \nu_i^{\nu_i}}{c^3} d\nu_i \cdot V$$

Now, Bose assumed that the volume of each allowed eigen state (i.e. each elementary cell) in the phase space is h^3 .

Therefore, the total n_i of allowed eigen states lying in the frequency range ν_i and $(\nu_i + d\nu_i)$ is given by,

$$\frac{G_{\nu_i} d\nu_i}{h^3} = \frac{4\pi \nu_i^{\nu_i} V}{c^3} d\nu_i \quad \text{--- (1)}$$

Since each photon has two independent directions of polarization, eqⁿ (1) is to be multiplied by a factor 2 to give the correct numbers of allowed states which are given by

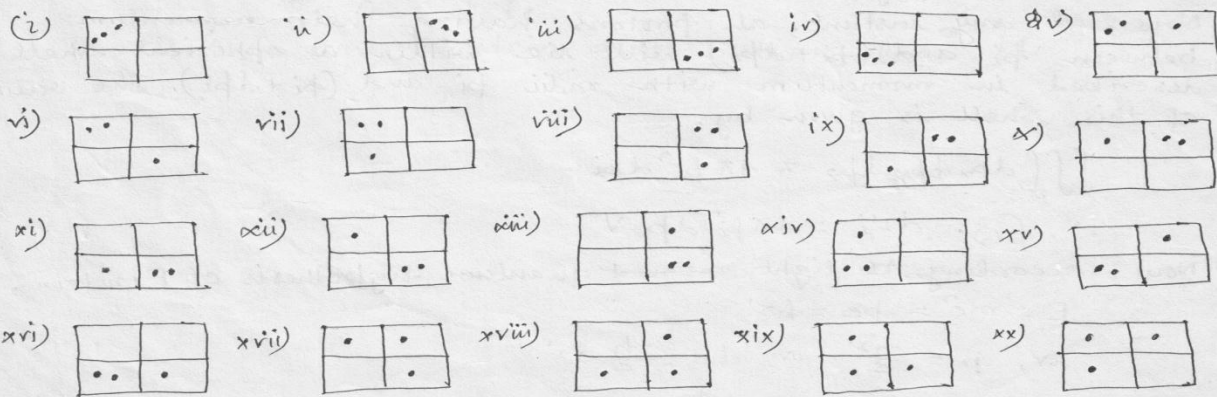
$$A_{\nu_i} d\nu_i = 2 \times \frac{G_{\nu_i} d\nu_i}{h^3}$$

$$= 2 \times \frac{4\pi \nu_i^{\nu_i} V}{c^3} d\nu_i$$

$$= \frac{8\pi \nu_i^2 V d\nu_i}{c^3} \equiv g_i$$

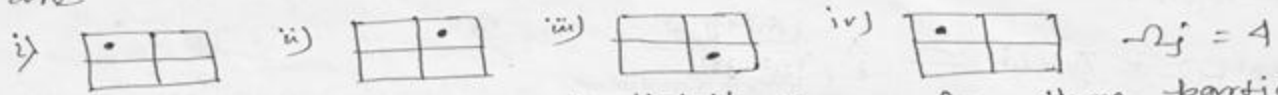
where g_i the degeneracy of the i^{th} energy level.

□ Let i^{th} energy level is 4 fold degenerate and 3 particles are distributed amongst them. The possible distributions are



$$\therefore \Omega_i = 20$$

Again let j^{th} energy level is also 4 fold degenerate and 1 particle are distributed amongst them. The possible distributions are

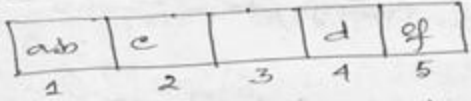


Therefore, the total no of distributions for three particles in i^{th} energy level and one particle in j^{th} energy level will be,

$$\Omega = \prod_i \Omega_i = 20 \times 4 = 80$$

Suppose, the i^{th} energy level is g_i fold degenerate and n_i particles are distributed amongst them. Now, let the states be designated by numbers, 1, 2, 3, ..., g_i and the particles are represented by letters, a, b, c, d, Suppose, a sequence begin with a number, e.g.

1 ab 2 c 3 4d 5ef



Now, after fixing a number in a sequence, there are $(n_i + g_i - 1)$ letters and numbers, which can be permuted amongst themselves. This can be done in $(n_i + g_i - 1)!$ ways. All these arrangements are not distinct. Out of these we reject those ways which merely permutes the n_i letters among themselves and the $(g_i - 1)$ numbers among themselves, since the particles and the partitions are indistinguishable. Thus the total numbers of distinct arrangements is given by

$$\Omega_i = \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

$$\therefore \Omega = \prod_i \Omega_i = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

where the product extends over all the energy levels.
 Now, as n_i and g_i are large, we may neglect 1.
 Therefore,

$$\Omega = \prod_i \Omega_i \approx \prod_i \frac{(n_i + g_i)}{n_i g_i}$$

$$\begin{aligned} \therefore \ln \Omega &= \sum_i [\ln (n_i + g_i) - \ln n_i - \ln g_i] \\ &= \sum_i [(n_i + g_i) \ln (n_i + g_i) - (n_i + g_i) \ln n_i + n_i \ln n_i + g_i \ln g_i - g_i \ln g_i] \\ &\quad \text{(using Stirling's approximation)} \end{aligned}$$

$$\ln \Omega = \sum_i [(n_i + g_i) \ln (n_i + g_i) - n_i \ln n_i - g_i \ln g_i]$$

Since Ω is maximum at eqm.

$$\therefore d\Omega = 0 \text{ or } d(\ln \Omega) = 0 \text{ at eqm.}$$

$$\therefore d \ln \Omega = \sum_i \left[\frac{n_i + g_i}{n_i + g_i} dn_i + \ln (n_i + g_i) dn_i - \frac{n_i}{n_i} dn_i - \ln n_i dn_i \right] = 0$$

$$\text{or, } d \ln \Omega = \sum_i [\ln (n_i + g_i) dn_i - \ln n_i dn_i] = 0$$

$$\text{or, } \sum_i \ln \frac{n_i + g_i}{n_i} dn_i = 0 \longrightarrow \textcircled{2}$$

Total energy of the system

$$E = \sum_i n_i \epsilon_i = \sum_i n_i h \nu_i$$

$$\begin{aligned} \therefore dE &= h \sum_i [\nu_i dn_i + n_i d\nu_i] \\ &= h \sum_i \nu_i dn_i = 0 \quad [\because \epsilon_i = h\nu_i = \text{const}] \end{aligned}$$

$$\text{or, } dE = \sum_i \nu_i dn_i = 0 \longrightarrow \textcircled{3}$$

(21)

Now we use the Lagrangian method of undetermined multipliers. For this purpose we multiply eqⁿ (3) by β and subtract eqⁿ (2), then

$$\sum_i [\beta \nu_i - \ln \frac{n_i + g_i}{n_i}] dn_i = 0$$

As the variation in dn_i is arbitrary, each term of the co-efficient of dn_i will vanish separately

$$\therefore \beta \nu_i - \ln \frac{n_i + g_i}{n_i} = 0$$

$$\text{or, } \boxed{\beta \nu_i = \ln \frac{n_i + g_i}{n_i}}$$

$$\therefore \frac{n_i + g_i}{n_i} = e^{\beta \nu_i}$$

$$\text{or, } 1 + \frac{g_i}{n_i} = e^{\beta \nu_i}$$

$$\text{or, } \frac{g_i}{n_i} = e^{\beta \nu_i} - 1$$

$$\text{or, } n_i = \frac{g_i}{e^{\beta \nu_i} - 1} \longrightarrow \textcircled{4}$$

Again we know, entropy $S = k \ln \Omega$

$$\text{or, } S = k \sum_i [(n_i + g_i) \ln (n_i + g_i) - n_i \ln n_i - g_i \ln g_i]$$

$$\frac{\partial S}{\partial n_i} = k \left[\frac{n_i + g_i}{n_i + g_i} + \ln (n_i + g_i) - \frac{n_i}{n_i} - \ln n_i \right]$$

$$= k [\ln (n_i + g_i) - \ln n_i]$$

$$= k \ln \frac{n_i + g_i}{n_i}$$

$$= k \beta \nu_i \quad \left[\because \ln \frac{n_i + g_i}{n_i} = \beta \nu_i \right]$$

$$\therefore \left(\frac{\partial S}{\partial n_i} \right) = k \beta \nu_i \longrightarrow \textcircled{5}$$

$$\text{Again } E = \sum_i n_i \epsilon_i = \sum_i n_i h \nu_i$$

$$\therefore \frac{\partial E}{\partial n_i} = h \nu_i$$

$$\therefore \frac{\partial S}{\partial E} = \frac{\partial S}{\partial n_i} \cdot \frac{\partial n_i}{\partial E} = k \beta \nu_i \cdot \frac{1}{h \nu_i} = \frac{k \beta}{h}$$

Again, from the combined first and second law, we know,

$$Tds = dE + PdV$$

$$\text{or, } ds = \frac{dE}{T} + \frac{P}{T} dV$$

$$\therefore \left(\frac{\partial S}{\partial E} \right)_V = \frac{1}{T}$$

\therefore We can write,

$$\frac{k\beta}{h} = \frac{1}{T}$$

$$\text{or } \boxed{\beta = \frac{h}{kT}}$$

From eqn (3) we get

$$n_i = \frac{g_i}{e^{\beta \epsilon_i} - 1} = \frac{g_i}{e^{\frac{h\nu_i}{kT}} - 1}$$

Now, putting the value of $g_i = \frac{8\pi\nu_i^2}{c^3} \cdot V \cdot d\nu_i$

$$\therefore n_i = \frac{\frac{8\pi\nu_i^2}{c^3} d\nu_i V}{e^{\frac{h\nu_i}{kT}} - 1} = \frac{8\pi\nu_i^2}{c^3} \cdot V \cdot \frac{d\nu_i}{e^{\frac{h\nu_i}{kT}} - 1}$$

$$\text{or, } \frac{n_i}{V} = \frac{8\pi\nu_i^2}{c^3} \cdot \frac{d\nu_i}{e^{\frac{h\nu_i}{kT}} - 1}$$

The left hand side of the above equation represents the number of photons per unit volume lying in the frequency range ν_i and $(\nu_i + d\nu_i)$. When it is multiplied by $h\nu_i$, the energy of photon, gives the energy density of radiation of frequencies between ν_i and $(\nu_i + d\nu_i)$,

$$\therefore U_{\nu_i} d\nu_i = \frac{n_i}{V} \times h\nu_i = \frac{8\pi h \nu_i^3}{c^3} \cdot \frac{d\nu_i}{e^{\frac{h\nu_i}{kT}} - 1}$$

This is Bose's formula of Planck's law.

Bose assumed photons are indistinguishable from one another and the photons constituting the photon gas may be created and destroyed and hence their number in a system is not necessarily constant. Because in every emission process in nature results in the creation of photons and if a photon of frequency ν is absorbed by the wall of the enclosure,

can be replaced by the emission of several photons of (22)
 frequencies ν_1, ν_2, \dots , provided the total energy of the
 system is constant i.e.

$$h\nu = h\nu_1 + h\nu_2 + \dots$$

Thus in this case, we have,

$$\sum_i dn_i \neq 0$$

But Einstein assumed that, the total number of photons
 is conserved i.e.

$$\sum_i n_i = \text{constant}$$

$$\text{or, } \sum_i dn_i = 0$$

$$\text{Now } \Omega = \prod_i \frac{(n_i + g_i - 1)}{n_i! g_i!}$$

$$\Rightarrow \prod_i \frac{(n_i + g_i)}{n_i! g_i!} \quad [\text{As } n_i \text{ and } g_i \text{ are large numbers, } 1 \text{ is neglected}]$$

$$\therefore \ln \Omega = \sum_i [\ln (n_i + g_i) - \ln n_i - \ln g_i]$$

Using Stirling's approximation, we get

$$\ln \Omega = \sum_i [(n_i + g_i) \ln (n_i + g_i) - (n_i + g_i) - n_i \ln n_i + n_i - g_i \ln g_i + g_i]$$

$$= \sum_i [(n_i + g_i) \ln (n_i + g_i) - n_i \ln n_i - g_i \ln g_i]$$

$$\therefore d \ln \Omega = \sum_i \left[\frac{n_i + g_i}{n_i + g_i} dn_i + \ln (n_i + g_i) dn_i - \frac{n_i}{n_i} dn_i - \ln n_i dn_i \right] = 0 \text{ at eqm.}$$

$$\text{or, } d \ln \Omega = \sum_i [\ln (n_i + g_i) dn_i - \ln n_i dn_i] = 0$$

$$= \sum_i \ln \frac{n_i + g_i}{n_i} dn_i = 0 \quad \text{--- (6)}$$

$$\text{Now according to Einstein, } \sum_i dn_i = 0 \quad \text{--- (7)}$$

and the total energy of the system.

$$E = \sum_i n_i \epsilon_i = \text{constant}$$

$$\text{or, } dE = \sum_i \epsilon_i dn_i = 0 \rightarrow \textcircled{8}$$

Now we use the Lagrangian method of undetermined multipliers. For this purpose, we multiply eqⁿ $\textcircled{7}$ by α and eqⁿ $\textcircled{8}$ by β and subtract eqⁿ $\textcircled{6}$, then

$$\sum_i (\alpha + \beta \epsilon_i - \ln \frac{n_i + g_i}{n_i}) dn_i = 0$$

As the variation of dn_i are independent of each others, each term of the co-efficient of dn_i will vanish separately.

$$\therefore \alpha + \beta \epsilon_i - \ln \frac{n_i + g_i}{n_i} = 0$$

$$\text{or, } \ln \frac{n_i + g_i}{n_i} = \alpha + \beta \epsilon_i$$

$$\text{or, } \frac{n_i + g_i}{n_i} = e^\alpha e^{\beta \epsilon_i}$$

$$\text{or, } \frac{g_i}{n_i} = e^\alpha e^{\beta \epsilon_i} - 1$$

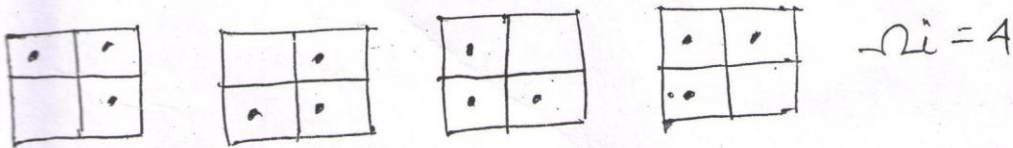
$$\text{or, } \boxed{n_i = \frac{g_i}{e^\alpha e^{\beta \epsilon_i} - 1}}$$

This is the Bose-Einstein distribution law

Fermi-Dirac statistics

This statistics is obeyed by indistinguishable particles of half-integral spin that have anti-symmetric wave function and obey Pauli-exclusion principle. The particles obey Pauli's exclusion principle according to which each quantum state or eigen state may contain 0 or 1 particle. Then obviously g_i must be greater than or equal to n_i . \Rightarrow

Let i th energy level is 4 fold degenerate and 3 particles are distributed amongst them. The no. of distinct arrangements are



Again, let j th energy level is also 4 fold degenerate and 1 particle is distributed amongst them. The no. of distinct arrangements are



therefore, the total no. of distinct arrangements for 3 particles in i^{th} energy level and one particle in j^{th} energy level will be,

$$\Omega = \prod_i \Omega_i = 4 \times 4 = 16$$

⇒ (v) Suppose the i^{th} energy level is g_i fold degenerate and n_i particles are distributed amongst them. We can select any one of the g_i states in g_i different ways and place one particle in it. One of the remaining $(g_i - 1)$ states we can choose one in $(g_i - 1)$ ways and place the second particle in it. Proceeding in this manner, the state for the last particle can be chosen in $(g_i - n_i + 1)$ ways. Thus, the total number of ways of selecting the states will be,

$$g_i(g_i-1)(g_i-2) \dots (g_i-n_i+1) \\ = \frac{g_i!}{(g_i-n_i)!}$$

Now, since the particles are indistinguishable, n_i ways of permutation of n_i particles does not give any new arrangement. Hence the number of realising the distribution of n_i particles in the g_i -states at the energy ϵ_i is,

$$n_i = \frac{g_i!}{(g_i-n_i)! n_i!} \quad [g_i, n_i]$$

$$\therefore \Omega = \prod_i n_i = \prod_i \frac{g_i!}{(g_i-n_i)! n_i!}$$

where the product extends over all the energy levels

$$\therefore \ln \Omega = \sum_i [\ln g_i! - \ln (g_i-n_i)! - \ln n_i!]$$

Now, using Stirling approximation, we have,

$$\ln \Omega = \sum_i [g_i \ln g_i - g_i - (g_i-n_i) \ln (g_i-n_i) + (g_i-n_i) - n_i \ln n_i + n_i]$$

$$= \sum_i [g_i \ln g_i - g_i - (g_i-n_i) \ln (g_i-n_i) + g_i - n_i - n_i \ln n_i + n_i]$$

$$= \sum_i [g_i \ln g_i - (g_i-n_i) \ln (g_i-n_i) - n_i \ln n_i]$$

Since Ω is maximum at equilibrium,

$$\therefore d\Omega = 0 \quad \text{or} \quad d(\ln \Omega) = 0 \quad \text{at eqm.}$$

$$\therefore d \ln \Omega = \sum_i \left[0 - \frac{g_i-n_i}{g_i-n_i} (-1) dn_i - \ln (g_i-n_i) (-) dn_i - \frac{n_i}{n_i} dn_i - \ln n_i dn_i \right] = 0$$

$$= \sum_i [dn_i + \ln (g_i-n_i) dn_i - dn_i - \ln n_i dn_i] = 0$$

$$= \sum_i \ln \frac{g_i-n_i}{n_i} dn_i = 0 \quad \rightarrow \text{①}$$

As the total number of particles of the system, n is constant (24)
 i.e. $n = \sum_i n_i = \text{constant}$

$$\therefore dn = \sum_i dn_i = 0 \rightarrow (2)$$

the total energy of the system, E is constant i.e.

$$E = \sum_i n_i \epsilon_i = \text{constant}$$

$$\therefore dE = \sum_i \epsilon_i dn_i = 0 \rightarrow (3)$$

we use the Lagrangian method of undetermined multipliers. For this purpose we multiply eqⁿ (2) by α and eqⁿ (3) by β and subtract eqⁿ (1), then,

$$\sum_i (\alpha + \beta \epsilon_i - \ln \frac{g_i - n_i}{n_i}) dn_i = 0$$

the variation of dn_i are independent of each other i.e. as the n_i are independent variables, each term of the co-efficient will vanish separately,

$$\therefore \alpha + \beta \epsilon_i - \ln \frac{g_i - n_i}{n_i} = 0$$

$$\text{or, } \ln \frac{g_i - n_i}{n_i} = \alpha + \beta \epsilon_i$$

$$\text{or, } \frac{g_i - n_i}{n_i} = e^{\alpha + \beta \epsilon_i}$$

$$\text{or, } \frac{g_i}{n_i} = e^{\alpha + \beta \epsilon_i} + 1$$

$$\text{or, } n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i} + 1}$$

this is Fermi-Dirac distribution formula.